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Solid State Structures of Some Dithionoamido-18-crown-6 Ligands

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The structures of three Dithionoamido-18-crown-6 ligands have been determined by X-ray diffraction studies. The results show that the carbon and oxygen atoms on the macroring opposite the pyridine ring are disordered. A serious conformation change is noted when methyl substituents are bonded to the amide nitrogen atoms.

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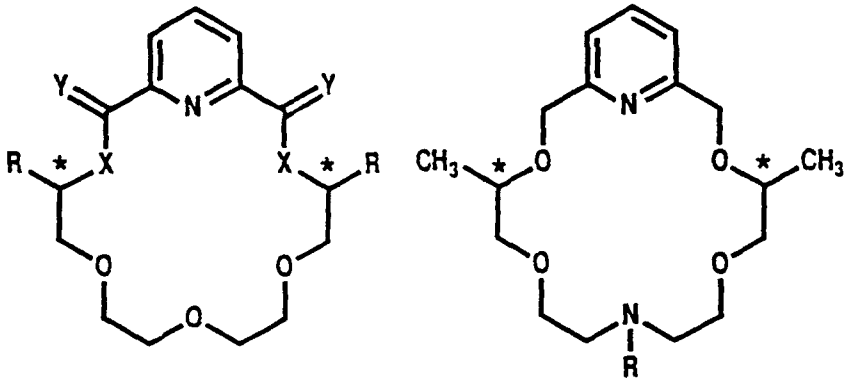
Figure 1. Chiral Diamido-, Dithionoamido-, Diaza- and Azapyridino-18-crown-6 Ligands



1, X = NH; Y = O; R = benzyl (*S,S*)
2, X = NH; Y = S; R = benzyl (*S,S*)
3, X = NH; Y = H_2; R = benzyl (*S,S*)
4, X = NH; Y = O; R = phenyl (*S,S*)
5, X = NH; Y = S; R = phenyl (*S,S*)
6, X = NH; Y = H_2; R = phenyl (*S,S*)
7, X = NCH_3; Y = O; R = phenyl (*S,S*)
8, X = NCH_3; Y = S; R = phenyl (*S,S*)
9, X = NCH_3; Y = H_2; R = phenyl (*S,S*)

10, R = H (*S,S*)
11, R = $C(O)CH_3$ (*S,S*)

The structures of **2**, **5**, and **8** were determined by X-ray diffraction studies. The discussion of the experimental procedures used in these studies and tables of structure determination summaries, atomic parameters, and torsion angles are included in the supplementary material. The molecule of **5** contained a 2-fold axis. The unit cells of both **5** and **8** contain two chemically similar but crystallographically distinct molecules of **5** and **8**. Unfortunately, the number of single crystal data for each structure was not sufficient for a full anisotropic refinement, but by blocking atoms so that the number of parameters to be refined in each block was not so large, it was possible to refine most of the non-hydrogen atoms of the three structures anisotropically. Specifically, all non-hydrogen atoms of **2**, all non-hydrogen atoms of one molecule of **5** and all non-

hydrogen atoms of the macrocyclic ring, pyridine ring, and the sulfur atom of both molecules of **8** were refined anisotropically. One molecule of **5**, which was badly disordered, and the methyl and phenyl carbon atoms of the two molecules of **8** were refined isotropically. The resulting *R* values were for **2**, R = 0.057, Rw = 0.0645; for **5**, R = 0.097, Rw = 0.085; and for **8**, R = 0.079, and Rw = 0.043. Details of the blocking of parameters and the treatment of hydrogen atoms of the three structures are contained in the supplementary material.

Computer drawings of the three molecules are shown in figures **2**, **3** and **4**. Only one of the two molecules of **5** and **8** were included as the conformations of the pairs are similar. These drawings clearly establish the structural formulas of the molecules, and also show the conformation of each molecule. In all three molecules, the 18-member ring is severely strained and deviates from the expected conformation of 18-crown-6 type molecules. This is established by the torsion angles listed in the supplementary material. This strain is expected because of the presence of the aromatic pyridine ring in the macrocyclic ring, and also the replacement of two of the oxygens of the ring by two nitrogens. As a result of these features, the carbon and oxygen atoms opposite the pyridine in the macrocyclic ring are disordered (see the thermal parameters for each structure in the supplementary materials). Perhaps the most interesting feature is the conformational change brought about by the presence of the methyl groups bonded to the nitrogens of the ether ring of **8**. This effect is shown in the deviations of the S and N atoms from the plane of the pyridine ring. The deviations of the nitrogen and sulfur atoms from the plane calculated for the pyridine and neighboring carbon atoms bonded to the pyridine are shown in Table II.

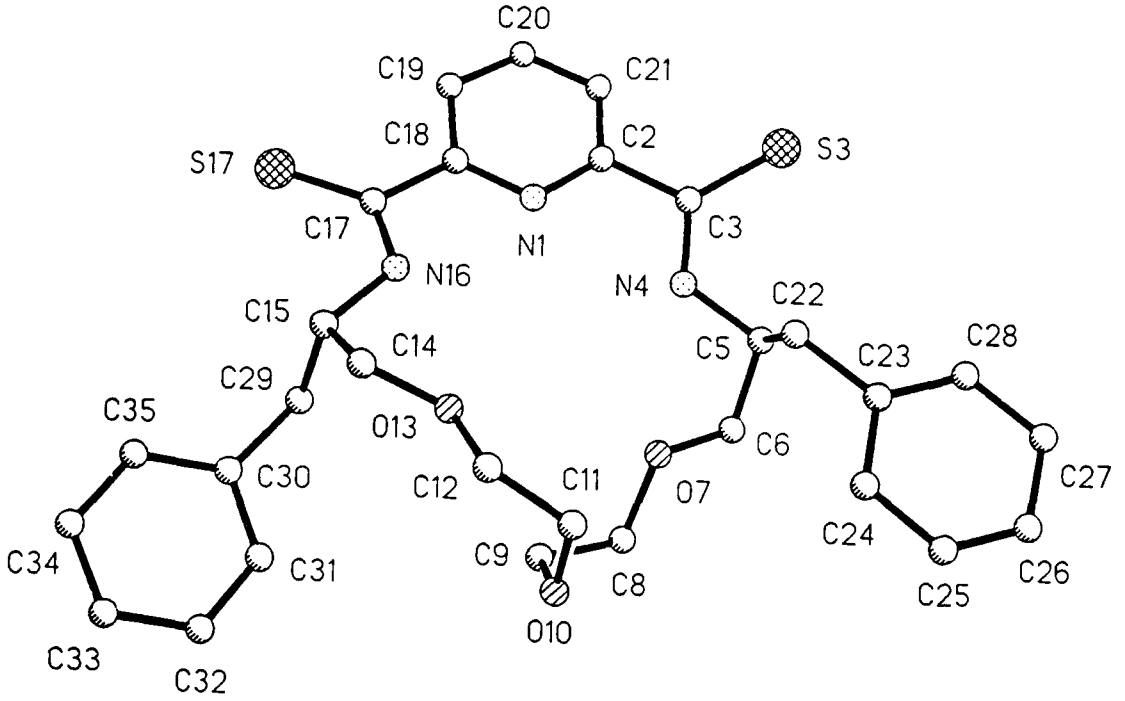


Figure 2. X-ray crystal structure of **2** drawn with SHLEXTL-PLUS.[39] Hydrogen atoms were omitted for clarity.

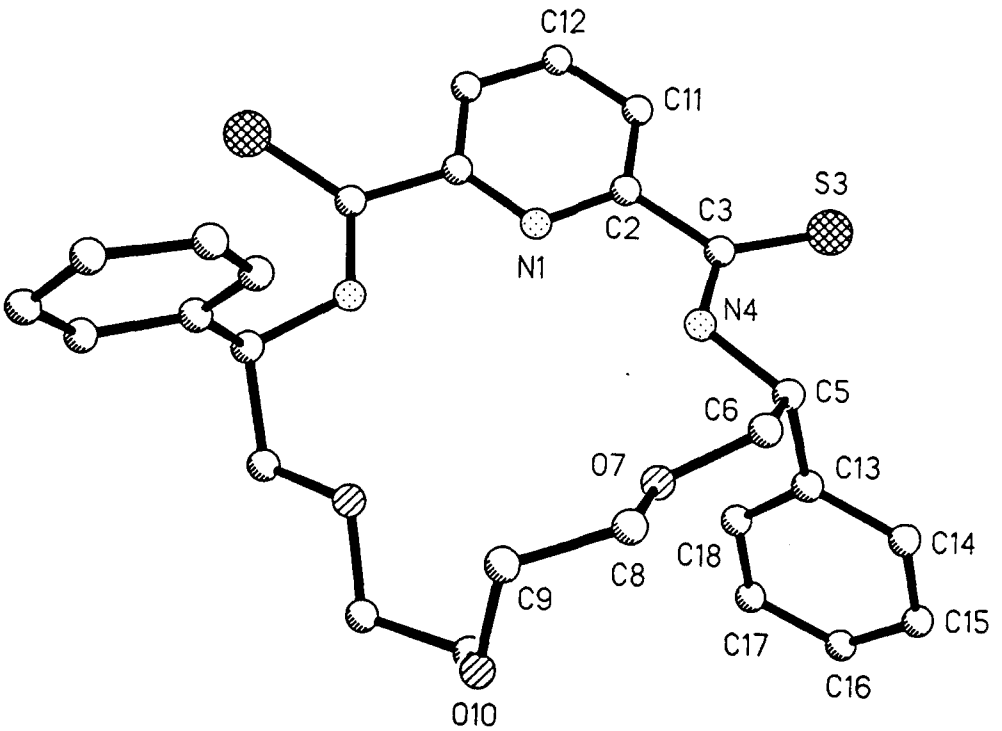


Figure 3. X-ray crystal structure of the unprimed molecule of **5** drawn with SHELXTL-PLUS.[39] The primed molecule and hydrogen atoms were omitted for clarity.

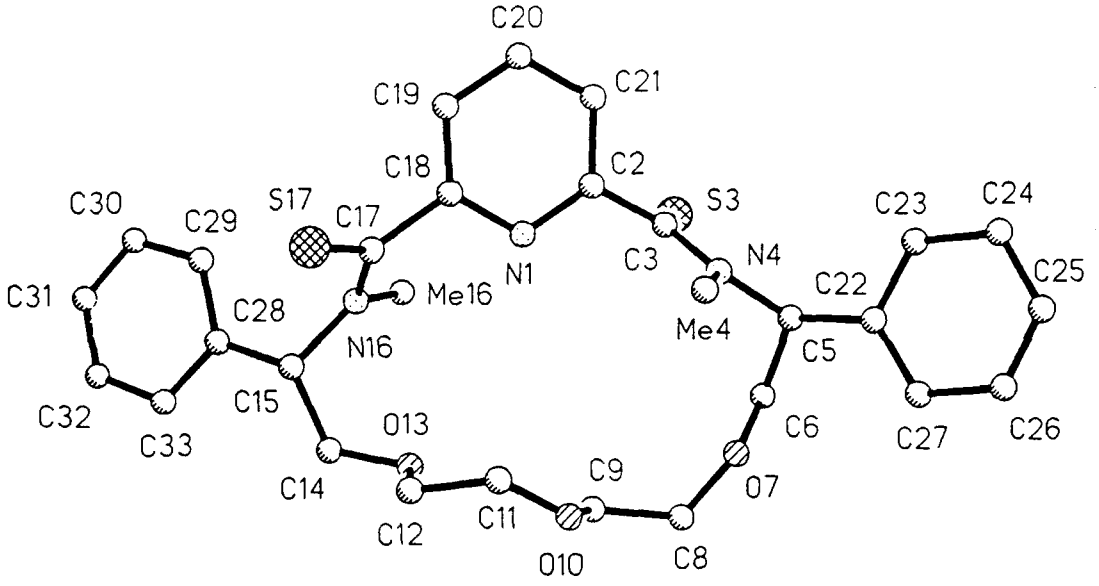


Figure 4. X-ray crystal structure of the unprimed molecule of **8** drawn with SHELXTL-PLUS.[39] The primed molecule and hydrogen atoms were omitted for clarity.

Table II. Deviation of Nitrogen and Sulfur Atoms from the Plane of the Pyridine and Neighboring Carbon Atoms

Molecule	Deviation of S(Å)		Deviation of N(Å)	
2	S3	0.46	N4	-0.39
	S17	-0.13	N16	0.21
5	S3	-0.20	N4	0.20
	S3'	-0.01	N4'	0.12
8	S3	-1.56	N4	1.02
	S17	1.16	N14	-0.90
	S3'	1.48	N4'	-0.99
	S17'	-1.21	N16'	1.02